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Effects of Ionizing Radiations on Aqueous

Solutions of Formic and Oxalic Acid


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## ABSTRACT

It has been shown that in aqueous solutions $CO_2$ and bicarbonate react with negatively charged polarons $(H_2O)^-$ formed by the irradiation of water by $\gamma$-rays, leading to the formation of $.CO_2^-$, i.e. the carboxyl radical ion.

In the presence of organic solutes, the carboxyl radical ion may add on to other free radicals, e.g. those formed by the action of radiation-produced OH radicals on organic solutes, to give the corresponding carboxylic acids.

Using C-14 labelled carbon dioxide or bicarbonate, this process could provide a method for the production of carboxylic acids labelled in the carboxyl group.

In neutral solutions two reducing species, i.e. negative polarons and primarily formed H atoms, have been shown to be present in irradiated water; their reactions with various solutes have been studied.

All irradiations were carried out with $Co^{60}$ $\gamma$-rays.

For irradiation of aqueous solutions in the presence and absence of different gases $(O_2, CO_2, N_2O)$ standard irradiation techniques have been used.

Analysis of the gaseous irradiation products has been carried out by means of the mass-spectrometer. Other irradiation products have been determined spectrophotometrically or by radioactive tracer techniques.

## INTRODUCTION

Although an appreciable amount of work has already been carried out with the object of establishing the nature of the primary reactive species produced by the action of ionizing radiation on water and on the mechanism of their reactions, a complete and satisfactory understanding has not, as yet, been achieved.

In the present work, special attention has been directed towards the irradiation of aqueous solutions of some relatively simple organic molecules such as formic acid, methanol, oxalic acid, etc., in the range pH 5 - 9. Particular attention has been given to the investigation of the nature and the yields of the different reducing species produced by the action of ionizing radiations on water.

From a chemical point of view, the distinction between the different primary species must be based on some specific reactions. In those cases where their reactions are similar, a differentiation may be obtained by means of two-solute systems. For instance, $O_2$ reacts rapidly with both the reducing species $(H_2O)^-$ and H-atoms and cannot therefore be used for their differentiation, and also the reaction product $(H_2O_2)$ is the same. However, as Allan and Scholes[1] have found, e.g. acetone can be used for this purpose; from experiments in this system, they have been able to show that in addition to polarons there is a primary formation of H-atoms in neutral solutions of $G\sim0.5$.

Search for other satisfactory scavengers has drawn attention to the possible uses of $CO_2$ and $N_2O$. We have found that $CO_2$ and bicarbonate

react readily with negative polarons, but relatively very slowly with H-atoms and OH radicals. It has been suggested[2] that $N_2O$ also reacts readily with the reducing species but not with OH radicals. The use of $N_2O$ by itself does not appear to be very satisfactory. On the other hand, we have found that $N_2O$ is very useful when used as a second solute; in many instances it may behave very similarly to $CO_2$.

## EXPERIMENTAL TECHNIQUES

All irradiations were carried out with $Co^{60}$ γ-rays. Radiation doses were measured by the Fricke dosimeter, assuming a value of $G(Fe^{III}) = 15\cdot5$ for $Co^{60}$ γ-rays.

Solutions for irradiation were prepared under conditions of the utmost purity. Water was purified by triple distillation. Ordinary distilled water was distilled from an alkaline potassium permanganate solution into a dilute phosphoric acid solution (0·1 ml. of concentrated phosphoric acid in 2 l.), from which it was further distilled into a pyrex flask. The pH of the water was usually in the range 5·3 to 5·7.

Most of the chemicals used were "Analar" grade. Sodium formate was recrystallised three times and dried in a vacuum desiccator over sodium hydroxide pellets. The middle fraction of methanol distillate was used. Carbon dioxide was prepared from sodium carbonate and sulphuric acid and purified by fractional distillation in vacuo. Medical grade of "British Oxygen" nitrous oxide was used, and also purified by fractional distillation in vacuo.

Standard irradiation techniques were used for irradiation of aqueous solutions in the presence and absence of different gases $(O_2, CO_2, N_2O)$. The irradiation vessels were made of pyrex.

Most of the analytical work was concerned with measurements on gaseous products. An apparatus for the collection and separation of semi-micro quantities of gases ($\cdot$01 to 1 cc.) has been constructed. The total amount of gaseous products was determined by PVT measurements, followed by mass-spectrometric analysis.

Spectrophotometric analysis was used for the detection of some products, such as $H_2O_2$, formaldehyde, glyoxylic acid, etc.

Carboxylic acids were determined by using C-14 tracer methods. The activities of the samples were measured by means of a Geiger-Muller counter. Labelled oxalic acid was determined by the addition of a certain amount of oxalic acid, to act as a carrier, and precipitation as calcium salt was carried out with a subsequent measurement of the activity of the samples. In some cases oxalic acid was determined gravimetrically as the calcium salt.

## EXPERIMENTAL RESULTS

In all irradiations yield-dose plots were obtained with at least 4 points and the proportionality of yields to radiation dose checked. In some cases (e.g. $H_2$ yields in irradiated formate solutions) the yield-dose plots were non-linear, presumably due to secondary reactions. In such cases, initial G-values (number of molecules per 100 eV absorbed) were

6.

taken into consideration.

Fig. 1 shows the concentration dependence of the hydrogen yield in
deaerated neutral sodium formate solution.

The formation of glyoxylic acid at higher formate concentrations was
not determined due to the interference by the formate.

Fig. 2 shows the hydrogen yield, $G(H_2)$, in deaerated 1 mM sodium
formate solution as a function of the concentration of added sodium bicar-
bonate.

In the presence of added oxalate the hydrogen yield drops to $G = 1.05$.

Fig. 3 shows $G(CO_2^-)$, i.e. the yield of the carboxyl group in oxalic
acid derived from the bicarbonate, as a function of the formate and bicar-
bonate concentration. C-14 labelled bicarbonate was used to differentiate
between carboxyl groups in the radiation-produced oxalic acid from bicar-
bonate and from formate.

Fig. 4 shows the pH-dependence of $G(H_2)$ from 10 mM formic acid solution
irradiated in vacuo and in the presence of 20 mM $CO_2$. The yield of $CO_2^-$ in
oxalic acid (from $C^{14}O_2$) is also given. pH was adjusted with $H_2SO_4$.

Fig. 5 shows yield-dose plots of radiation products in neutral aqueous
solution of $N_2O$. The concentration of $N_2O$ was 17 mM. The positive inter-
cept of the $N_2$ line is due to very small amounts of $N_2$ from the irradiated
glass.

Fig. 6 shows the dependence of the gaseous yields in neutral aqueous
solutions of methanol and $N_2O$ on the concentration of methanol. The
yield-dose plots for hydrogen peroxide are non-linear but deviate less
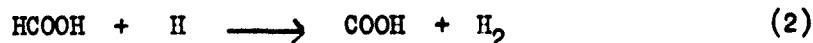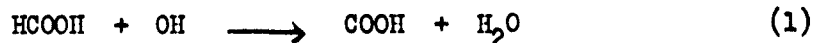from linearity with increasing methanol concentration.

Fig. 7 shows the dependence of the gaseous yields in neutral solution of sodium formate and $N_2O$ on the concentration of formate.
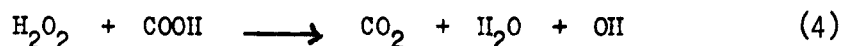
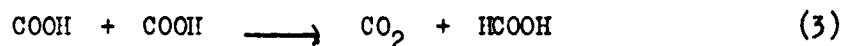Irradiation of aqueous solution of deuterated sodium formate in the presence of $N_2O$ gives rise to hydrogen ($H_2$) and deuterium hydride (HD). The yield of hydrogen, $G(H_2)$ = 0·4, is independent of formate concentration over the range $10^{-3}$ - $10^{-1}$ M.

As there is no suitable analytical method for micro-quantities of oxalic acid, we have irradiated aqueous solutions of sodium formate in the presence of sodium bicarbonate and $N_2O$ using very high doses ($2 - 7 \times 10^{19}$ eV/ml). The yield of oxalic acid has been determined gravimetrically as the calcium salt. Under these conditions, the yield of oxalic acid depends on the concentration of formate and only slightly on the dose; initial values could not be determined and G-values for a dose of $2 \times 10^{19}$ eV/ml are given. These oxalic acid yields were found to be: G = 3·03 in $5 \times 10^{-1}$ M HCOONa with $5 \times 10^{1}$ M NaHCO$_3$, and G = 3·2 in $10^{-1}$ M HCOONa and 1atm. $N_2O$, and G = 3·4 in $5 \times 10^{-1}$ M HCOONa and 1 atm. $N_2O$.

## DISCUSSION

In acid solution, where formic acid exists in the unionized form, the following sequence of reactions is envisaged:

$$HCOOH + OH \longrightarrow COOH + H_2O \tag{1}$$

$$HCOOH + H \longrightarrow COOH + H_2 \tag{2}$$

$$COOH + COOH \longrightarrow CO_2 + HCOOH \tag{3}$$

$$H_2O_2 + COOH \longrightarrow CO_2 + H_2O + OH \tag{4}$$

H-atoms are formed _via_ the process:

$$H_3O^+ + (H_2O)^- \longrightarrow H + aq. \tag{5}$$

The lower yield of $H_2$ ($G = 3 \cdot 2$) could be explained assuming that reaction (6):

$$H + H_2O_2 \longrightarrow H_2O + OH \tag{6}$$

plays a more important role than reaction (4). The initial yields probably represent the full yield, as is indicated by the results of Czapski, Rabani and Stein[3].

Hydrogen yields are dependent to some extent on the relative concentrations of formic and sulphuric acids (Fig. 4). This could be explained by:

$$HSO_4^- + OH \longrightarrow HSO_4 + OH^- \tag{7}$$

$$HSO_4 + H \longrightarrow H_2SO_4 \tag{8}$$
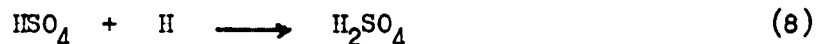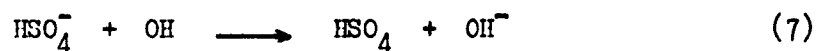
The influence of sulphuric acid has been observed by many workers.

In the presence of $CO_2$ (Fig. 4), $G(H_2)$ is markedly lower and depends on pH and relative concentrations of formic acid and $CO_2$. It is important to note that at higher pH the $G(H_2)$ drops to $0 \cdot 95$, the value also obtained in the presence of bicarbonate. The drop in hydrogen yield is due to reaction (9):
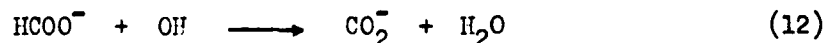
$$CO_2 + (H_2O)^- \longrightarrow CO_2^- + H_2O \tag{9}$$
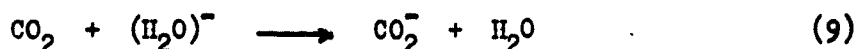
which competes with reaction (5).

The carboxyl radical, $CO_2^-$, may undergo the reaction:

$$CO_2^- + H_3O^+ \longrightarrow COOH + H_2O \qquad (10)$$
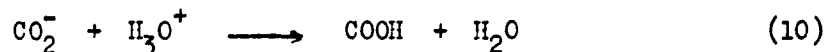
or recombine, giving oxalic acid, viz.

$$2\ CO_2^- \longrightarrow \begin{array}{c} COO^- \\ | \\ COO^- \end{array} \qquad (11)$$

In neutral solution, formic acid is present in the ionized form, and the following reaction takes place:

$$HCOO^- + OH \longrightarrow CO_2^- + H_2O \qquad (12)$$

Reaction (10) then is negligible and only reaction (11) takes place. The formation of oxalic acid has been observed by a few authors[4]. The fate of $(H_2O)^-$ has not been satisfactorily explained. Garrison et al.[5] suggested as a general reaction:

$$2\ H_2O^- \longrightarrow H_2 + 2\ OH^- \qquad (13)$$
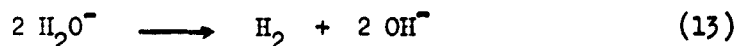
which cannot be accepted on the basis of our results. We have found that in the case of deuterated formate, the hydrogen yield is composed of $H_2$ as well as HD. $G(H_2)$ was found to be very nearly equal to the molecular hydrogen yield, though slightly higher, possibly due to isotopic impurity. of the deuterated formate. On the same grounds, the sequence[5]

$$H_2O + e \longrightarrow H^- + OH \qquad (14)$$

$$H^- + H_2O \longrightarrow H_2 + OH^- \qquad (15)$$
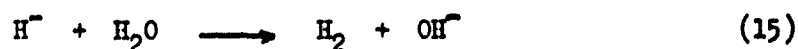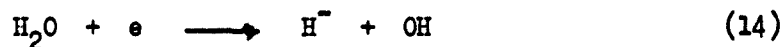
cannot be accepted.

The fact that the total hydrogen yield is in excess of the molecular yield (see Fig. 1) could be explained in the following way:
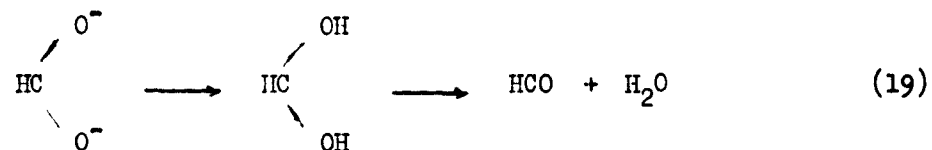
$$G(H_2) \;=\; G_{H_2} \;+\; G_{H_a} \;+\; G_H \tag{16}$$

where $G(H_2)$ represents the total hydrogen yield; $G_{H_2}$, the molecular hydrogen yield; $G_{H_a}$, the yield of hydrogen atoms formed directly[6]; and $G_H$, the yield of hydrogen atoms formed by reaction (5) or possibly by a small contribution from
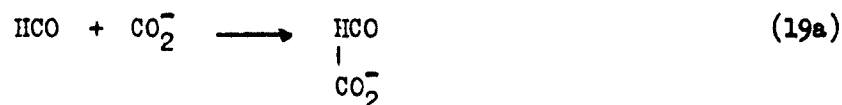
$$(H_2O)^- \;\longrightarrow\; H \;+\; OH^- \tag{17}$$
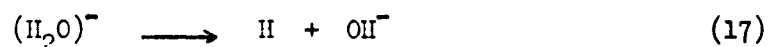
One has further to assume that the reaction:

$$HCOO^- \;+\; (H_2O)^- \;\longrightarrow\; H - C \overset{\displaystyle O^-}{\underset{\displaystyle O^-}{\big<}} \tag{18}$$
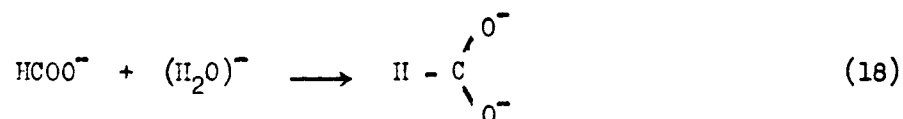
takes part to some extent though it must be very slow. The free radical formed in this way represents the hydrated carbonyl radical and the step
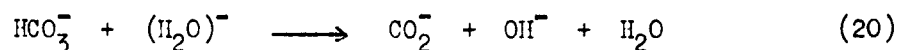
$$HC \overset{\displaystyle O^-}{\underset{\displaystyle O^-}{\big<}} \;\longrightarrow\; HC \overset{\displaystyle OH}{\underset{\displaystyle OH}{\big<}} \;\longrightarrow\; HCO \;+\; H_2O \tag{19}$$

which leads to the formation of glyoxylic acid according to:

$$HCO \;+\; CO_2^- \;\longrightarrow\; \underset{\displaystyle CO_2^-}{\overset{\displaystyle HCO}{|}} \tag{19a}$$

The decrease of $G(H_2)$ (Fig. 1) could be explained by competition between reactions (5), (17) and (18).

In the presence of bicarbonate, $G(H_2)$ decreases in formate solution (Fig. 2). The decrease is probably due to

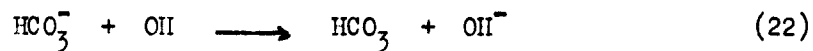$$HCO_3^- + (H_2O)^- \longrightarrow CO_2^- + OH^- + H_2O \qquad (20)$$

One may argue that the bicarbonate ion does not react with negative polarons and that reaction (20) should be replaced by the reaction with $CO_2$ which is in equilibrium with the bicarbonate ion according to:
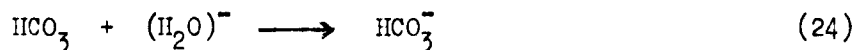
$$HCO_3^- + H_3O^+ \rightleftharpoons H_2CO_3 \rightleftharpoons CO_2 + H_2O \qquad (21)$$
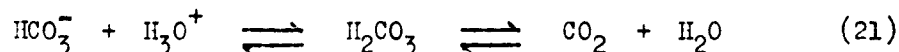
$G_{H_\alpha}$ is more or less constant due to the very low reactivity of $H_\alpha$ either with bicarbonate ion or $CO_2$ and the high reactivity of $H_\alpha$ with formate ion; the relatively long plateau in Fig. 2 is evidence for this.

The carboxyl radical arising from reaction (20) could be differentiated from the one coming from formate (according to reaction 12) by the use of $NaHC^{14}O_3$. The contribution of the bicarbonate towards oxalic acid formation is then represented by the C-14 labelled radioactive oxalic acid. The dependence of $G(C^{14}O_2^-)$ on the concentrations of formate and bicarbonate is shown in Fig. 3. The increased yield for higher concentrations of formate and bicarbonate could be explained on the basis of the increased scavenging of the primary species (negative polarons) which would otherwise undergo recombination.

In bicarbonate solutions, the formation of oxalic acid does not take place. Molecular hydrogen is fully protected and the molecular hydrogen peroxide has the value of $G = 0.45$. These results would indicate the following mechanism:
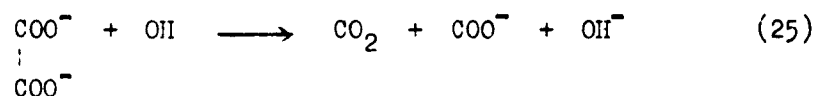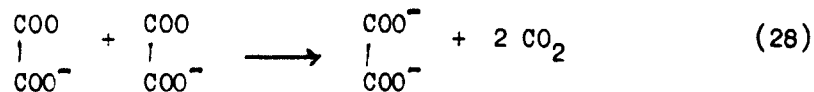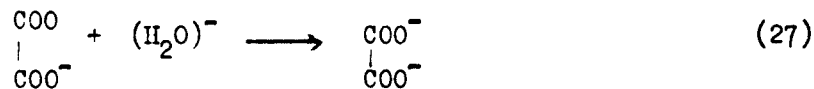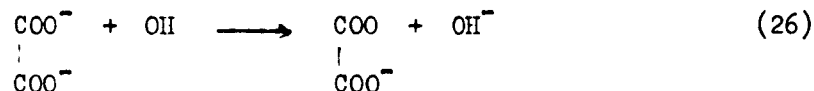
$$HCO_3^- + OH \longrightarrow HCO_3 + OH^- \tag{22}$$

$$CO_2^- + HCO_3 \longrightarrow CO_2 + HCO_3^- \tag{23}$$

The reaction

$$HCO_3 + (H_2O)^- \longrightarrow HCO_3^- \tag{24}$$
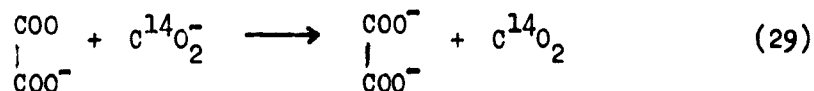
may possibly take place besides or instead of reaction (23).

In the system $(C^{14}O_2 + \text{oxalate})$, formation of labelled oxalic acid could not be detected and therefore the reaction[7]:

$$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix} + OH \longrightarrow CO_2 + COO^- + OH^- \tag{25}$$

has to be ruled out. A probable mechanism appears to be:

$$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix} + OH \longrightarrow \begin{matrix} COO \\ | \\ COO^- \end{matrix} + OH^- \tag{26}$$

$$\begin{matrix} COO \\ | \\ COO^- \end{matrix} + (H_2O)^- \longrightarrow \begin{matrix} COO^- \\ | \\ COO^- \end{matrix} \tag{27}$$

$$\begin{matrix} COO \\ | \\ COO^- \end{matrix} + \begin{matrix} COO \\ | \\ COO^- \end{matrix} \longrightarrow \begin{matrix} COO^- \\ | \\ COO^- \end{matrix} + 2\ CO_2 \tag{28}$$

In the presence of $C^{14}O_2$, reaction (27) is replaced by:

$$\begin{matrix} COO \\ | \\ COO^- \end{matrix} + C^{14}O_2^- \longrightarrow \begin{matrix} COO^- \\ | \\ COO^- \end{matrix} + C^{14}O_2 \tag{29}$$
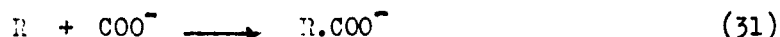
In formate solutions, in the presence of oxalate, $G_H$ disappears _via_ reaction (27), resulting in an apparent decrease in $G(H_2)$.

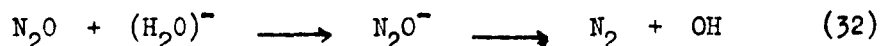In general, carboxylation takes place when free organic radicals are present:

$$RH + OH \longrightarrow R + H_2O \tag{30}$$

followed by:

$$R + COO^- \longrightarrow R.COO^- \tag{31}$$
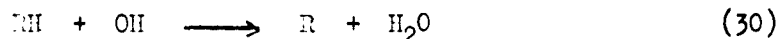
Reaction (31) is much faster than reaction (11). Therefore, formation of oxalic acid does not take place in the presence of free organic radicals. Various substrates have been successfully carboxylated[8].

In the case of a solute which can accept polarons, the relative concentrations of solute and $CO_2$, or bicarbonate, have to be adjusted according to the relative rate constants for the polaron reactions.

It has been suggested[2] that $N_2O$ can react with the reducing species, converting them into OH radicals. In a neutral solution of nitrous oxide (cf. Fig. 5) the following reactions are envisaged:

$$N_2O + (H_2O)^- \longrightarrow N_2O^- \longrightarrow N_2 + OH \tag{32}$$

$$H_2 + OH \longrightarrow H_2O + H \tag{33}$$

$$H + OH \longrightarrow H_2O \tag{34}$$

$$H_2O_2 + OH \longrightarrow H_2O + HO_2 \tag{35}$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \tag{36}$$

$$OH + OH \longrightarrow H_2O_2 \tag{37}$$

The low stationary yields of $H_2$ and $H_2O_2$ which we have found are in agreement with this mechanism, whereas Dainton and Peterson's results, which indicate protection of both hydrogen and hydrogen peroxide, cannot be explained because reaction (37) is much slower than reactions (33) and (35). $G(H_2) = 3 \cdot 1$ indicates the yield of negative polarons. On the basis of these results, one has to assume a very high reactivity of $H_2O$ with negative polarons.

In the methanol + $N_2O$ solutions (Fig. 6), the yield of $H_2$ remains virtually the same. The oxygen formed (reactions 35 and 36) disappears because the reaction

$$CH_3OH \;+\; OH \;\longrightarrow\; CH_2OH \;+\; H_2O \tag{38}$$
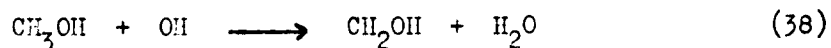
predominates.

Reactions (33) and (35) also disappear and the molecular hydrogen and hydrogen peroxide yields are fully protected. According to reaction (16), the hydrogen yield is represented by

$$G(H_2) \;=\; G_{H_2} \;+\; G_{H_\alpha} \tag{39}$$

$G_{H_\alpha}$ is dependent to some extent on the concentration of the OH scavenger, probably due to the recombination

$$H \;+\; OH \;\longrightarrow\; H_2O \tag{40}$$

Similarity between $CO_2$ and $N_2O$ is evident. Negative polarons react very fast with $N_2O$ and reactions (5) and (17) cannot compete efficiently in neutral solution. The reaction

$$N_2O + H \longrightarrow N_2 + OH \tag{41}$$
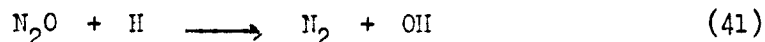
is a slow one and cannot efficiently compete with the reaction
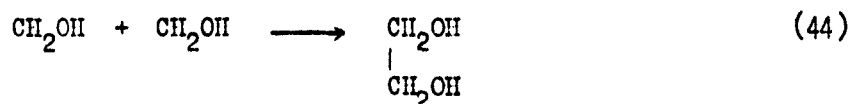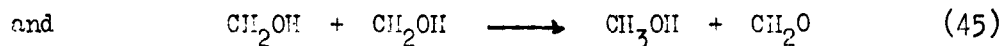
$$RH + H \longrightarrow R + H_2 \tag{42}$$
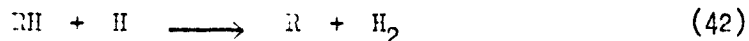
The nature of $H_\alpha$ is not quite clear; it shows some characteristics of an H-atom, but at the same time it could possibly represent an excited water molecule, $H_2O^*$, reacting in the same manner as an H-atom (as has been indicated by Dainton[6]), viz.

$$RH + H_2O^* \longrightarrow R + H_2 + OH \tag{43}$$
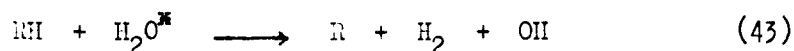
$H_\alpha$ does not appear in the kinetic considerations of Czapski and Allen[9] and on the basis of their results they rule out the existence of independently produced H-atoms. Hayon[10], in an attempt to reconcile his previous results (Hayon and Allen[11]), assumes quenching of the excited water molecule by oxygen, and according to him, $H_\alpha$ can appear in oxygen-free solution only. This hypothesis is in direct contradiction with the results of Hummel and Allen[12], who find in aqueous solution of ethanol saturated with air or oxygen, $G(H_2) > G_{H_2}$. The apparent non-existence of $H_\alpha$ in the inorganic systems must have some other explanation, e.g. reaction (40) or a similar reaction.

As has been shown, the reaction mechanism in methanol solution is very simplified, in the presence of $N_2O$. All the polarons ($G = 3 \cdot 1$) react with $N_2O$, viz. (32). The reaction (38) is followed by:

$$CH_2OH + CH_2OH \longrightarrow \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \tag{44}$$

and $\qquad$ $CH_2OH + CH_2OH \longrightarrow CH_3OH + CH_2O$ $\qquad$ (45)

G-values of 3·2 and 0·4 for ethylene glycol and formaldehyde respectively have been found[13], which supports the proposed mechanism.

In formate-$N_2O$ systems, the $G(H_2)$ is slightly higher than in $H_2O$ and methanol-$N_2O$ systems. Initial yields of oxalic acid could not be measured. The G(oxalate) = 3·4 in $5 \times 10^{-1}$ M formate + $N_2O$ (1atm.), though not fully 'initial', indicates an increase in radical yield $(G_R = 6·8)$. A chain reaction

$$CO_2^- + N_2O \longrightarrow CO_2 + N_2O^-$$ $\qquad$ (46)
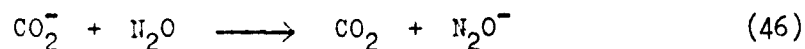
could possibly take place, but it should not be dependent on the concentration of formate. The measurement of the initial G-value for the formation of oxalic acid could give a definite answer.

On the basis of our results, the radiolysis of water and aqueous solutions by γ-rays should be represented, viz.

$$H_2O \longrightarrow H_2, \ H_2O_2, \ OH, \ (H_2O)^-, \ H_\alpha$$ $\qquad$ (47)
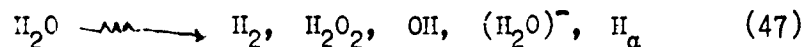
where $H_2$ and $H_2O_2$ represent molecular hydrogen and molecular hydrogen peroxide; OH, the free hydroxyl radical; and $(H_2O)^-$ and $H_\alpha$, the reducing species.

## FUTURE WORK

Having established further the existence of two primary reducing species, viz. the negative polarons $(H_2O)^-$ and H-atoms, in irradiated (deaerated) neutral aqueous solutions, our intention is to study the relative rates of the reactions of these species with different organic solutes.

It is also hoped, using the systems we have studied, to get more accurate assessments of the actual yields of the reducing species produced in the primary radiolysis of water and aqueous systems.

<u>Annex to Final Technical Report</u>

<u>Contract No. DA-91-591-EUC-1977</u>


Mr. Mionir Simic was employed as Research Associate under this contract. There have been no further administrative actions or changes in research policies. No important property was acquired at contract expense.

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12) Hummel, and Allen, Rad. Res., __17__, 307 (1962).

13) Munday, Scholes, Simic and Weiss, unpublished results.
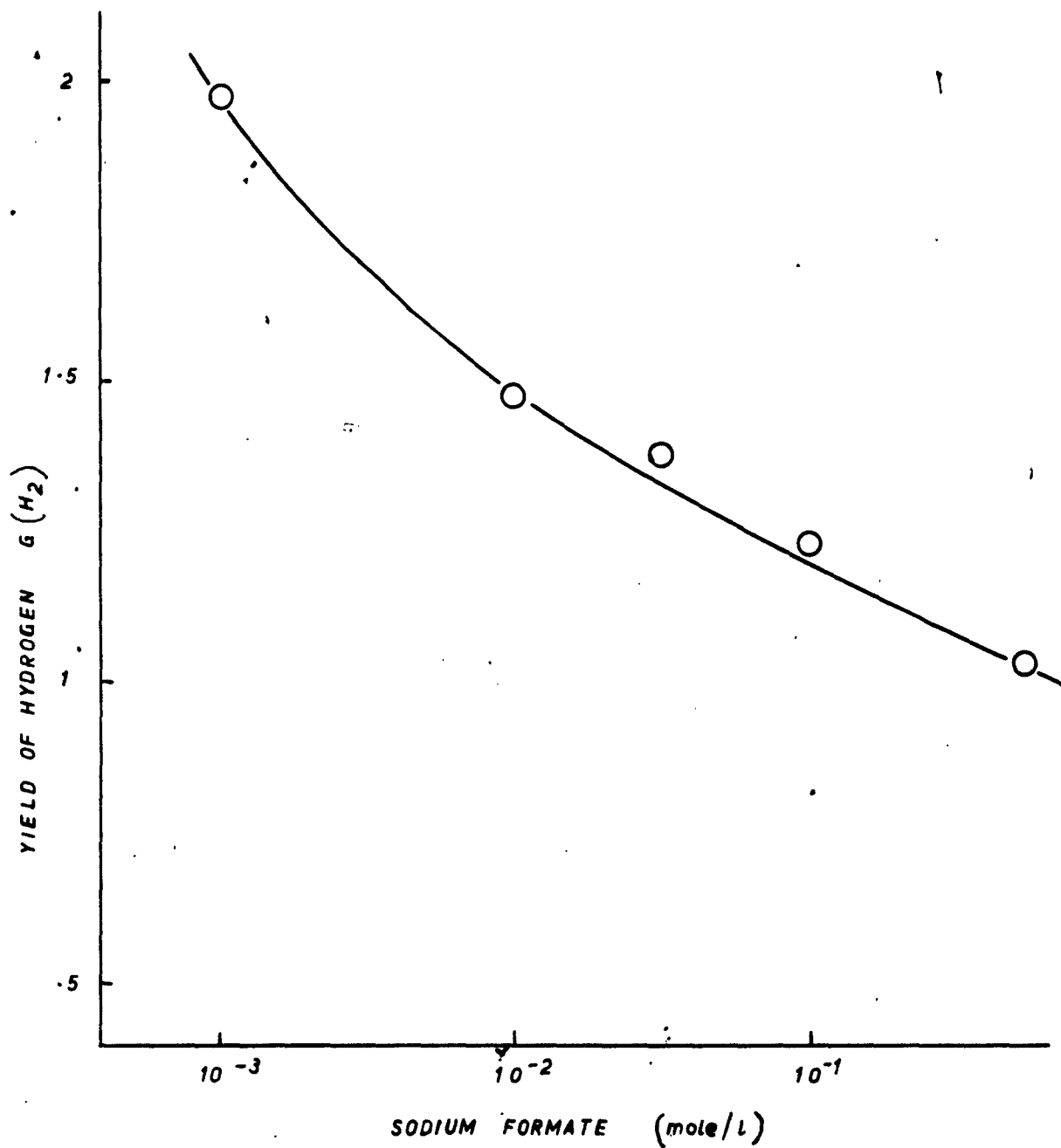
Fig 1. Irradiation ($Co^{60}$ γ-rays) of deaerated aqueous solutions of sodium formate. Dependence of the hydrogen yield on the concentration of formate.
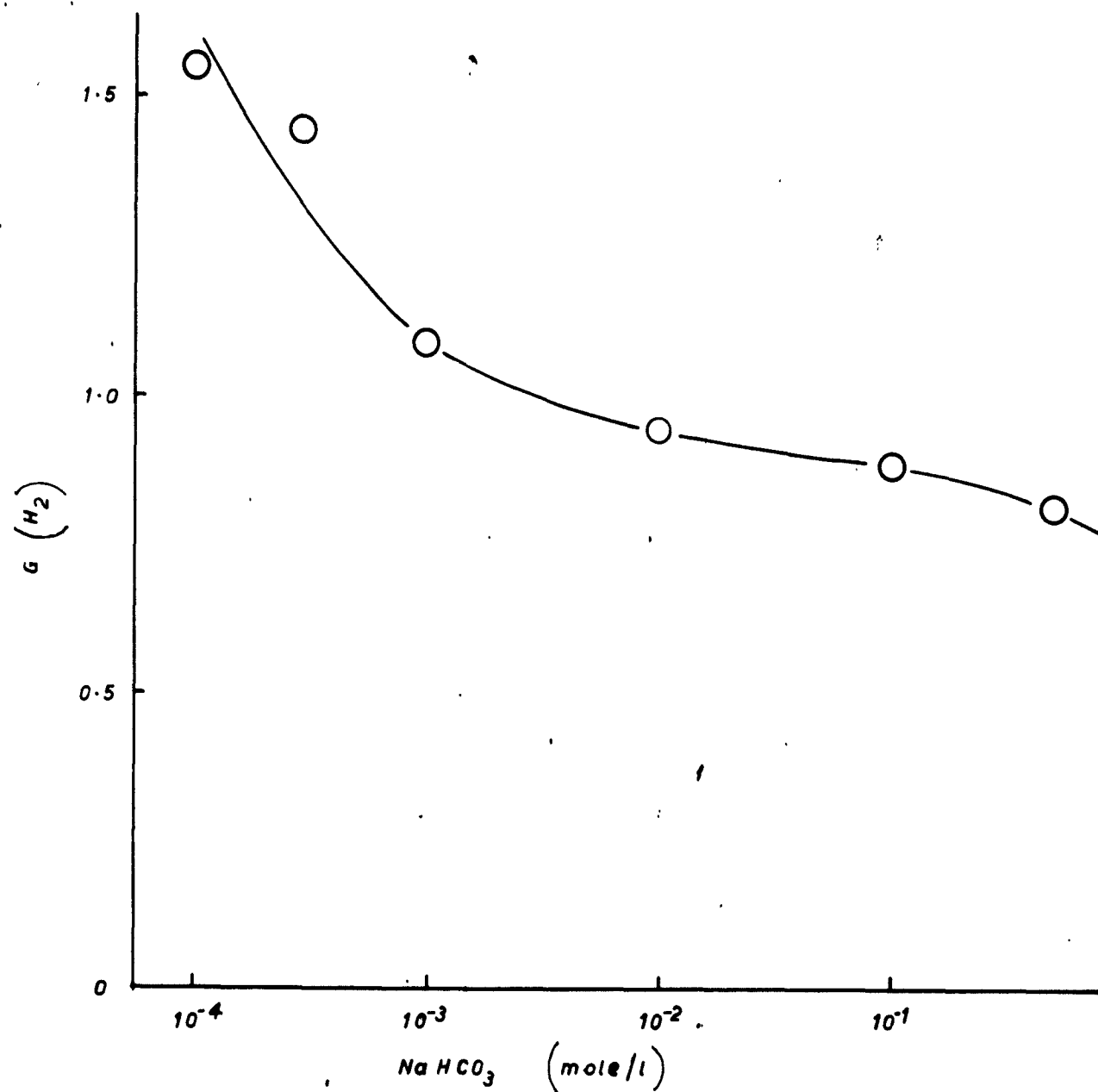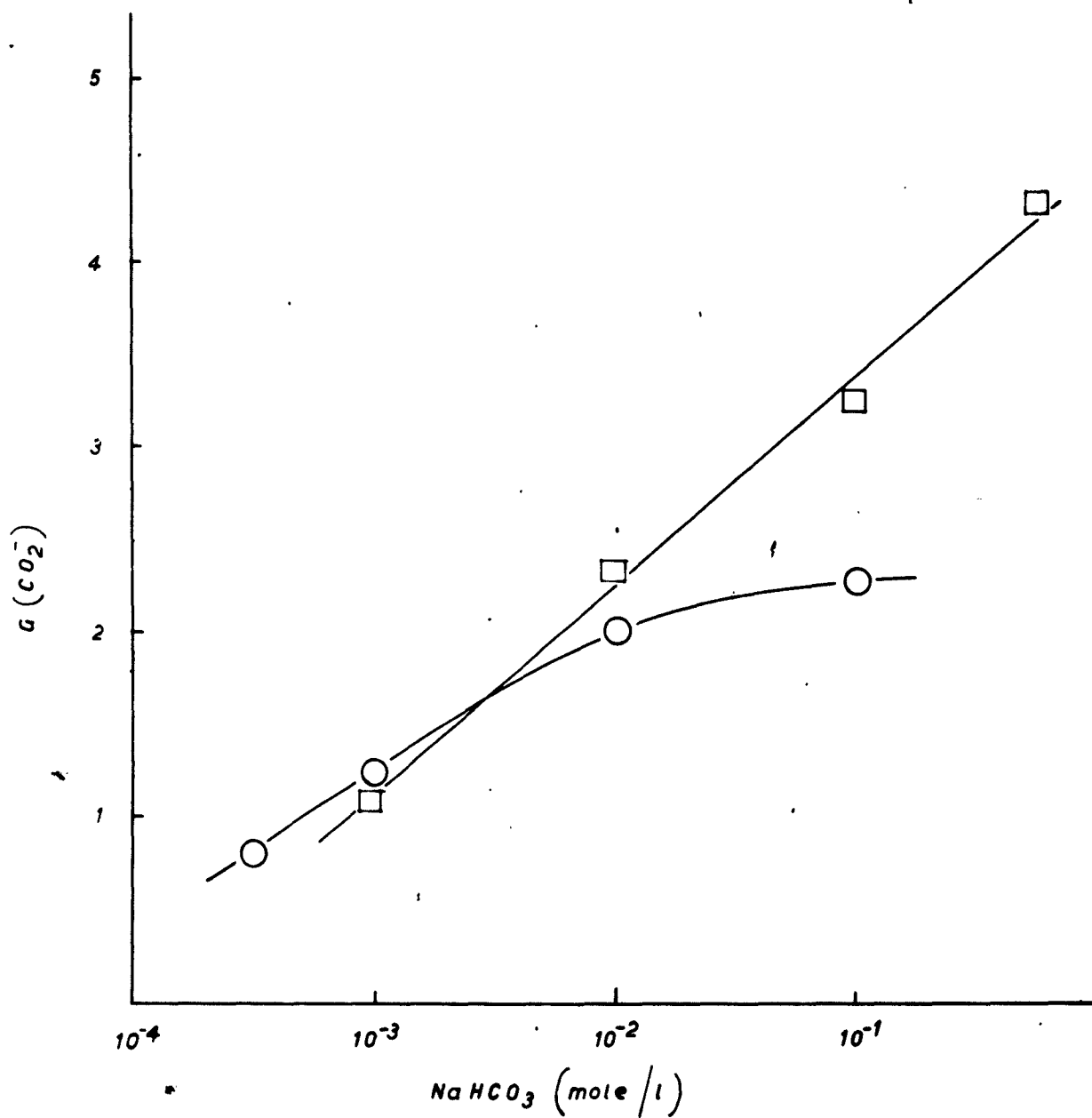
Fig. 2   Irradiation (Co⁶⁰ γ-rays) of deaerated aqueous solutions of 1 mM sodium formate in the presence of sodium bicarbonate. Dependence of the hydrogen yield on the concentration of bicarbonate.

Fig. 3    Irradiation ($Co^{60}$ $\gamma$-rays) of deaerated aqueous solutions of sodium formate in the presence of sodium bicarbonate. Dependence of the yield of C-14 labelled carboxyl group in oxalic acid on the concentration of C-14 labelled bicarbonate. O $\underline{10^{-3} \text{ M formate}}$; □ $\underline{10^{-1} \text{ M formate}}$.
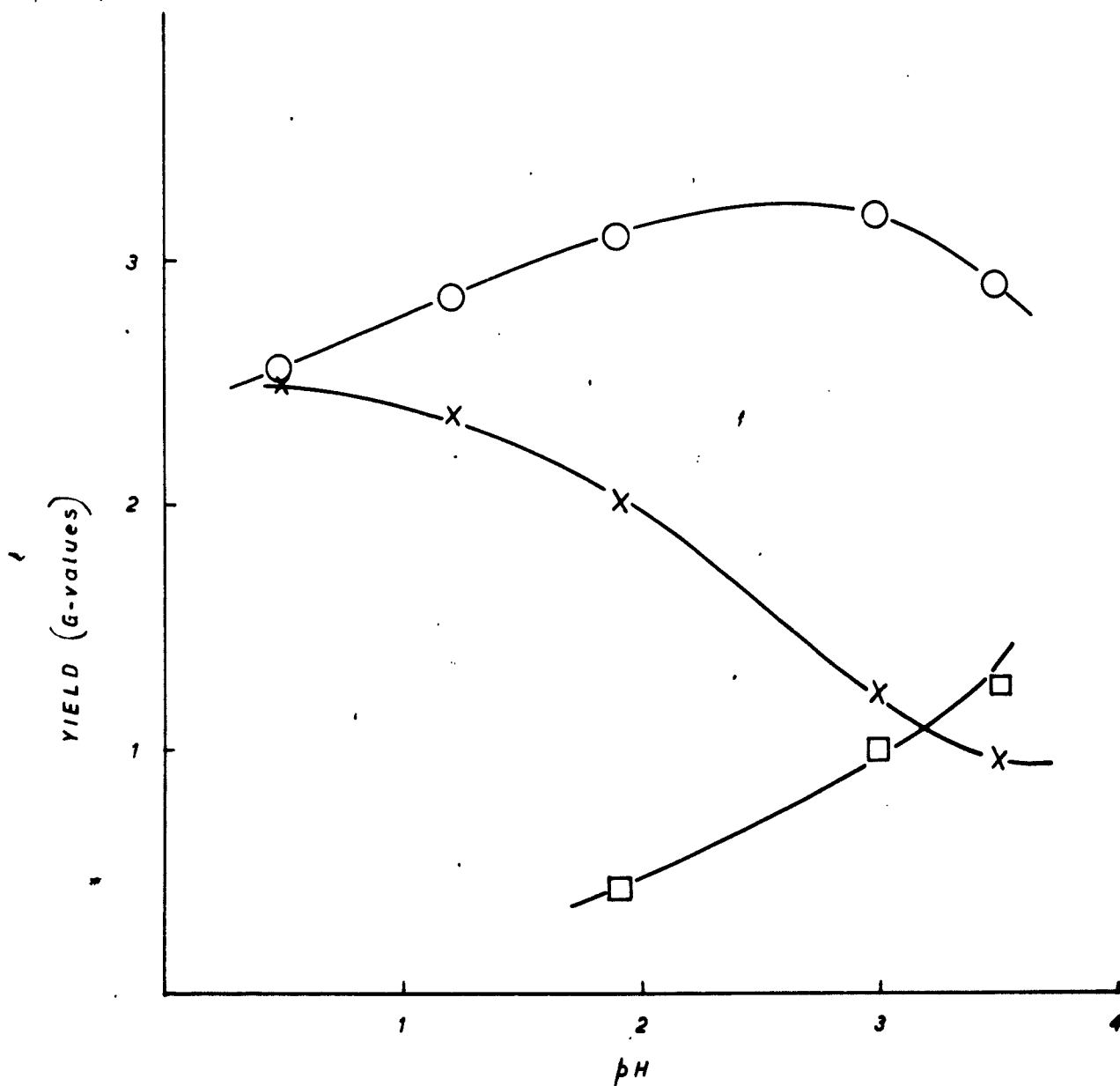
Fig 4    Irradiation (Co[60] $\gamma$-rays) of aqueous solutions of $10^{-2}$ M formic acid.    pH-dependence of the yield of   O  hydrogen in vacuum; X hydrogen in the presence of 2 x $10^{-2}$ M $CO_2$; ☐ C-14 labelled carboxyl group in oxalic acid from $C^{14}O_2$.
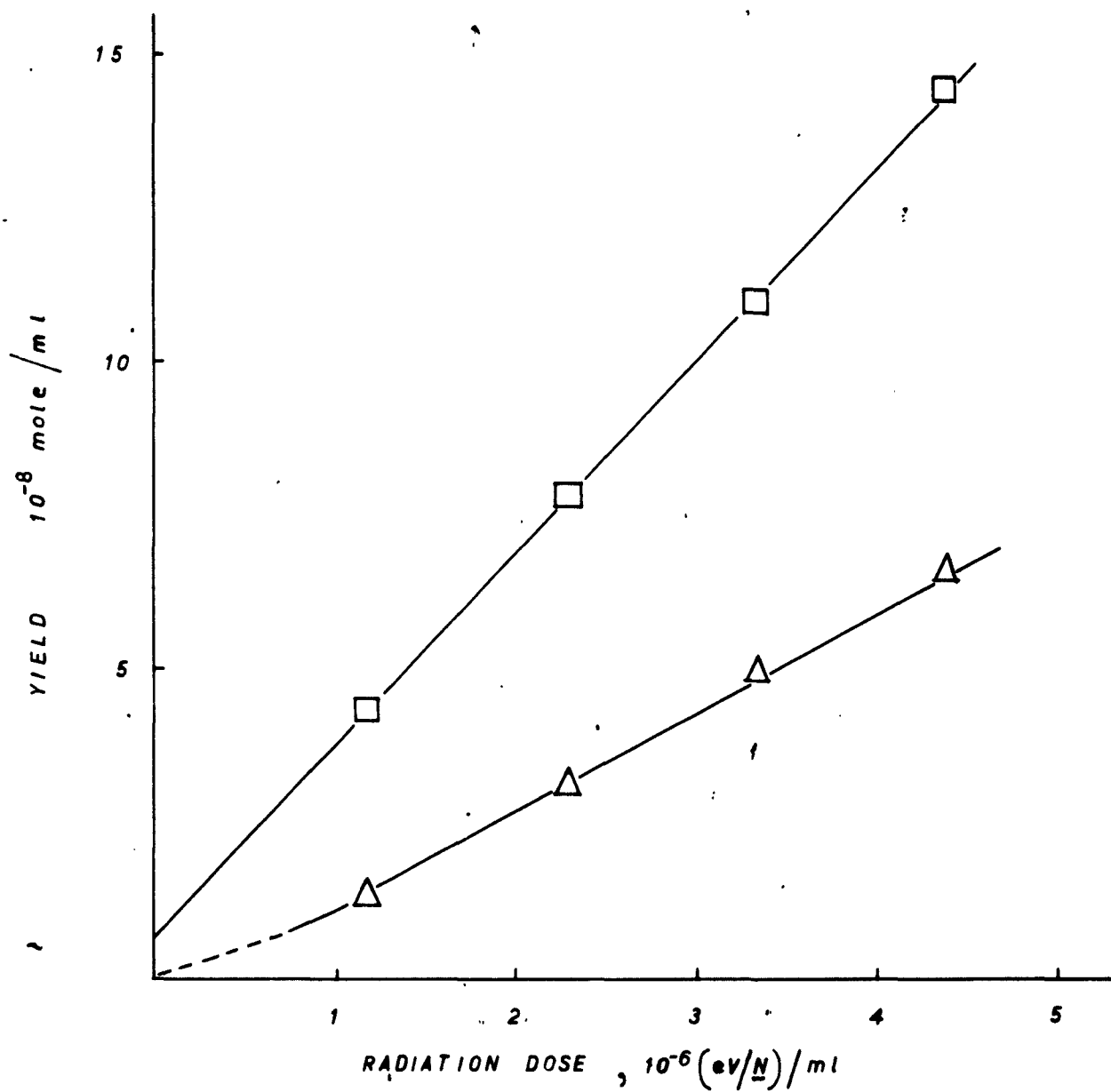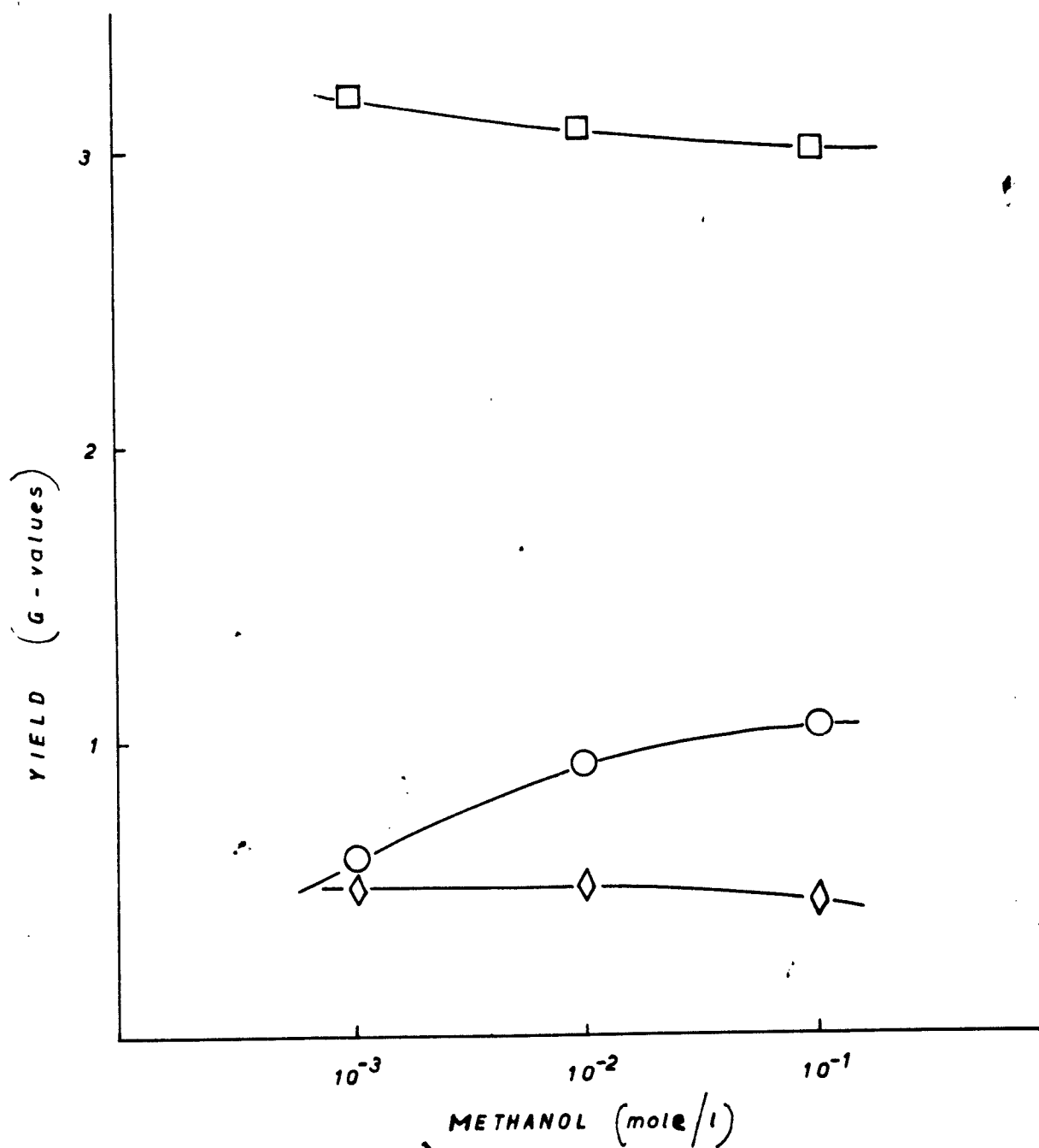
Fig. 5. Irradiation ($Co^{60}$ $\gamma$-rays) of aqueous solutions of 17 mM $N_2O$. Yield vs. dose plot of ☐ nitrogen; △ oxygen.

Fig. 6    Irradiation (Co$^{60}$ γ-rays) of aqueous solutions of methanol in the presence of 17 mM N$_2$O.    Dependence of the yield of ☐ nitrogen; O hydrogen; ◇ hydrogen peroxide, on the concentration of methanol.
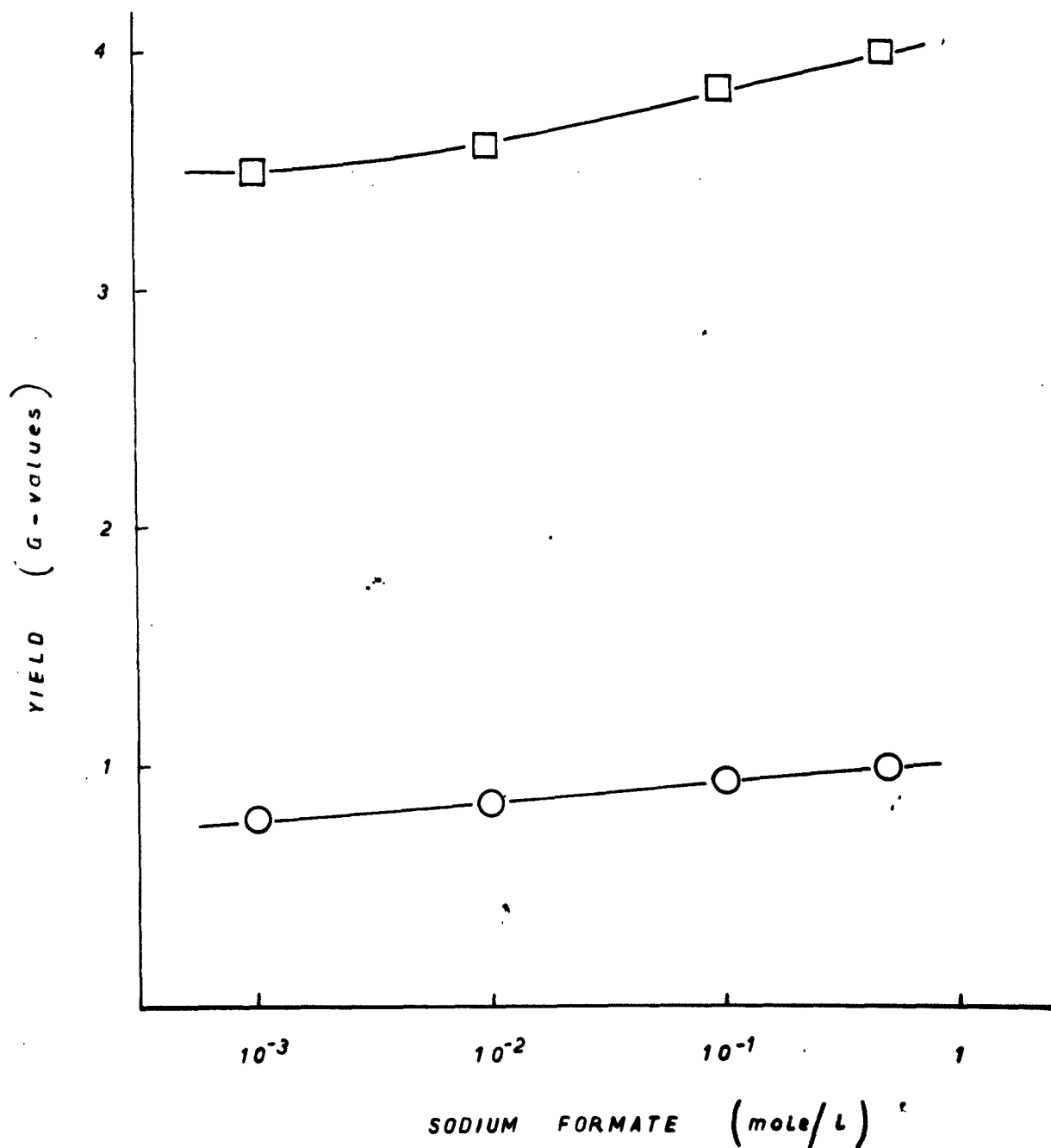
Fig 7. Irradiation (Co⁶⁰ γ-rays) of aqueous solutions of sodium formate in the presence of 17 mM $N_2O$. Dependence of the yield of ☐ nitrogen, and O hydrogen on the concentration of formate.